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(54) **Electroless nickel-boron plating.**

(57) The boron content of an electroless nickel-boron deposit is enhanced by including in the bath a source of zirconyl ions or vanadyl ions, which bath can be operated at moderate temperature and pH despite the fact that boranes can be used as reducing agents. The deposit laid down has a boron content of at least about 2 weight %, based on the total weight of the deposit. The source of the ions may be for example zirconyl chloride, vanadyl sulfate or sodium metavanadate at a concentration between 0.001 and 0.1 mol per liter of the bath.

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ELECTROLESS NICKEL-BORON PLATING

This invention generally relates to forming electroless nickel-boron deposits having a high boron content.

5 It has long been known that an electroless codeposit of nickel and boron is achieved by immersion of a substrate into an electroless bath including a source of nickel ions and a borane reducing agent. Often, it is desirable to lay down a deposit that has a relatively high boron content in order to enhance the hardness of the deposit when compared with a substantially pure nickel deposit of up to 99.9% nickel. Traditionally, however, borane-reduced baths form a codeposit that has severe limitations from the point of view of the ability to control the percentage of boron that could be laid down in the codeposit, borane-reduced baths being especially unsuitable for forming codeposits having a relatively high boron content on the order of 2 weight % and above. These borane-reduced deposits are limited generally by the pH of the bath and the stability of the borane reducing agent of the bath.

15 More particularly, as the pH of a borane-reduced bath is decreased, the percentage of boron codeposited with the nickel is increased; however, because boranes undergo hydrolysis at low pH values, borane reducing agents begin to lose their stability and thus are rapidly consumed as the bath pH is reduced below 4. A borane-reduced electroless nickel bath that will lay down a deposit having a high boron

content would have to be at a low pH, but a low pH bath consumes the borane reducing agent at an excessive rate that is unacceptable commercially. Therefore, while the boron content of borane-reduced codeposits could be increased by decreasing the pH, this capability is limited by the fact that the boranes are consumed at rates that are unacceptable commercially when the pH is lowered to a level that produces a high-boron codeposit. Generally, a borane-reduced bath that is commercially viable from the point of view of acceptable levels of borane consumption should have a pH well in excess of 5.

It is known that the boron content of nickel boron electroless deposits can be increased by the use of a borohydride ion as the reducing agent in the bath rather than a borane reducing agent, but borohydride-reduced baths lay down high-boron deposits only when such baths are operated at a pH of over 13 and at a temperature in excess of 90°C. These are relatively harsh conditions that are undesirable to maintain in a commercial electroless plating operation. But, if a borohydride-reduced bath is allowed to drop to a pH of below about 12, the bath undergoes spontaneous solution decomposition.

By the present invention, there has been discovered a manner of achieving the high boron percentage of above about 2% boron in the deposit from a borane-reduced electroless deposition bath, which avoids the use of the borohydride ion and avoids the high pH and high temperature conditions

associated therewith. Baths according to this invention are borane reduced and can be operated under a relatively moderate temperature and a moderate pH.

It is accordingly a general object of the present invention to provide improved electroless nickel boron plating, characterized by a nickel-boron codeposit having a relatively high boron content, while using a borane reducing agent.

According to the present invention, electroless nickel-boron plating is deposited from baths including zirconyl ions, vanadyl ions, or combinations or mixtures thereof, together with a borane reducing agent and a source of nickel. Other typical electroless nickel bath ingredients may be included, such as complexing agents, stabilizers, buffers, and the like.

It is believed that the boron deposition enhancers impart added stability to the borane reducing agent in the bath while also enhancing its boron depositing capabilities at moderate pH values. Zirconyl ion boron deposition enhancers can be added to the bath by any compound that will liberate zirconyl ions ( $\text{ZrO}^{++}$ ), such as zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ). Vanadyl ion ( $\text{VO}^{++}$ ) boron deposition enhancers can be provided by compounds such as vanadyl sulfate or vanadium oxysulfate ( $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ ) or other vanadyl salts, as well as by vanadates such as sodium metavanadate ( $\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$ ), which vanadates oxidize organic compounds within the bath and in turn themselves undergo

reduction to provide vanadyl ions within the bath.

The compounds which yield to zirconyl and/or vanadyl ions are included within baths at a concentration having a lower limit at which the particular enhancer increases the boron deposit percentage and an upper limit guided by economic and bath solubility considerations. A typical concentration of the boron deposition enhancer within the bath is at least about 0.0005 mol per liter, preferably at least about 0.0007 mol per liter, and most preferably at least about 0.001 mol per liter. Usually, there is no need to include these boron deposition enhancers at bath concentrations in excess of 0.5 mol per liter, preferably not greater than 0.1 mol per liter.

Borane reducing agents utilized in baths according to this invention include any bath-soluble borane source such as ammine boranes, amine boranes, lower alkyl substituted amine boranes, and nitrogen-inclusive heterocyclic boranes including pyridine borane and morpholine borane. Generally, the alkyl amine boranes are preferred, especially dimethylamine borane. Reducing agent concentrations within these baths are those that are sufficient to effect adequate reduction and are also cost-efficient for reducing the nickel cations within the bath. Typical minimum concentrations are at least about 0.001 mol per liter of bath, more usually at least about 0.005 mol per liter, while as much as 1 mol per liter could be included, and usually no more than about 0.1 mol per liter need be included.

Sources of nickel for these baths are bath soluble nickel salts such as the sulfates, chlorides, sulfamates, or other anions compatible with electroless nickel systems. Concentrations utilized are those that are typical for electroless nickel plating baths, on the order of between about 0.001 mol per liter of bath and about 0.5 mol per liter.

As is the case for most electroless nickel baths, these baths will often include complexing agents, and almost any type of complexing agent is suitable and can be selected depending upon considerations such as availability, economics, and properties desired for the particular bath in addition to that of increased boron content of the deposit laid down by the bath. Complexing agents are, generally speaking, bath soluble carboxylic acids and bath soluble derivatives thereof, including hydroxy-substituted carboxylic acids, amino-substituted carboxylic acids, and bath soluble derivatives thereof including anhydrides, salts or esters that are bath soluble. Other complexing agents include ester complexes of polyhydric compounds formed by reacting an oxyacid with a polyhydric acid or alcohol such as those described in Mallory United States Letters Patent No.4019910. Other complexing agents include pyrophosphoric acid and its derivatives as well as organo-phosphoric complexing agents including phosphonates.

Specific hydroxy substituted carboxylic acid complexing agents include citric acid, glycolic acid, lactic

acid and malic acid, while exemplary amino-substituted carboxylic acid complexing agents include  $\beta$ -alanine, aminoacetic acid, aminodiacetic acid, and the amino acids such as  $\alpha$ -alanine, aspartic acid, glutamic acid, glycine, leucine, 5 serrine, threonine, and valine. Complexing agents falling within the category of ester complexes of oxyacids and polyhydric acids or alcohols include ester complexes prepared by reacting an oxyacid with a carboxylic acid or alcohol compound which contains at least two hydroxy groups and from 10 about 4 to about 15 carbon atoms per molecule. Typical suitable polyhydric compounds include carboxylic acids such as tartaric acid, gluconic acid or glucoheptonic acid, and alcohols such as mannitol, 2,3-butanediol and 1,2,3-propanetriol. The oxyacids used in forming the ester are 15 generally inorganic acids such as boric, tungstic, molybdic or chromic acids. Usually, such ester complexes are in the form of a polyester that is an ester complex formed by reacting two or more mols of the oxyacid with one mole of the polyhydric compound.

20       Phosphonate complexing agents include aminotri(methylenephosphonic acid) and salts thereof such as a solution of the pentasodium salt of aminotri(methylene-phosphonate), 1-hydroxyethylidene-1,1-diphosphonic acid and salts thereof such as the trisodium salt of 25 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine tetra(methylphosphonic acid) and salts thereof, and 1,6-diaminohexane tetra(methylphosphonic acid) and the alkaline

metal and ammonium salts thereof.

Complexing agent bath concentrations will, of course, be somewhat dependent upon whatever particular complexing agent or agents are included within the bath. Generally speaking, complexing agents within the bath are at a concentration of at least about 0.0005 mol per liter and can be as high as bath solubility limits and economic considerations dictate, usually no higher than about 1.5 mol per liter. A typical range is between about 0.005 and about 1 mol per liter of bath, preferably between about 0.1 and 0.7 mol per liter, especially when the complexing agent is a carboxylic acid.

These baths may optionally include stabilizers such as those of the carboxylic acid type, sources of antimony or of lead for controlling the sulfide ion content, or a sulfur containing compound such as thiourea or a combination thereof such as thiodiglycolic acid. Whenever a sulfur-containing compound is added, the sulfur content must be carefully controlled, since excessive sulfur will reduce the boron content of the deposit. Any such sulfur addition should be monitored so that the maximum sulfur concentration is about 20 ppm as divalent sulfur. Otherwise, when stabilizers are added to the bath, they are at a concentration typical for the particular compound.

Other compositions that may be included in this system at their typical bath concentrations include buffers, buffering systems, codeposition enhancers, and pH adjusting



compounds such as strong bases. Polyalloy deposition may be accomplished by including bath-soluble compounds such as a complexing agent that is an ester complex prepared by reacting a polyhydric acid or alcohol with an oxyacid of the metal to be deposited as part of the polyalloy with nickel and boron or other metal.

In proceeding with the method according to this invention, a nickel-boron codeposit having a high boron content is laid down by deposition from a borane-reduced electroless nickel bath having a moderate pH and a moderate temperature, which bath includes a source of zirconyl and/or vanadyl ions. The operational pH is less than 13, typically between 4 and 10, and, in order to take the greatest advantage of the capabilities of this method to proceed under moderate conditions while still forming a high boron deposit, preferably the bath pH is maintained between about 5 and 7 while the temperature is maintained below 90°C, typically between about 60 and about 70°C. By such a method, nickel from the nickel source in the bath codeposits with boron from the reducing agent, this codeposit including in excess of 2 weight % boron, based on the total weight of the deposit.

The method includes preparing an electroless deposition bath including a bath-soluble source of nickel, a bath-soluble borane reducing agent, a boron deposition enhancer that liberates vanadyl ions and/or zirconyl ions when added to the bath, preferably in combination with an electroless bath complexing agent. Preparing the bath may

optionally include adding one or more stabilizers, sulfide-content controllers, buffers, buffering systems, polyalloy deposition sources, codeposition enhancers, and the like.

Typically, it will be necessary to adjust the pH of the bath  
5 to within the desired moderate pH range, which is usually a strong base such as hydroxide to the bath, or when the pH becomes too high by adding a strong acid, such as sulfuric acid or other mineral acids.

Substrates to be deposited are immersed in the bath  
10 thus prepared. The weight or thickness of the nickel-boron codeposit laid down by the bath will vary, of course, with the plating rate and the length of time that the substrate is immersed within the bath. Plating rates according to this method are between about 0.2 and about 0.5 mil per hour, and  
15 typical tank loadings are between about 0.25 and 1.0 square foot per gallon of bath.

Products produced according to this invention include substrates, both metal and non-metal, that are plated with a protective coating of an electroless nickel-boron codeposit  
20 having a boron content of at least about 2 weight %, which codeposit is laid down by a bath according to this invention. These products can have boron contents as high as or in excess of 5 weight %, based on the weight of the deposit. Usually, the balance of the deposit will be nickel. Such  
25 plated codeposits exhibit an enhanced hardness, on the order of from 800 to 1000 VHN<sub>50</sub>.

The following examples are offered to illustrate the present invention.

EXAMPLE I

An electroless bath was prepared to include 0.3 mol per liter of lactic acid, 0.08 mol per liter of citric acid, 0.04 mol per liter of dimethylamine borane, 0.01 mol per liter of zirconyl chloride octahydrate, 0.01 mol per liter of nickel, and enough ammonium hydroxide to maintain the pH at 6.0. The bath was raised to a temperature of 65°C, and a substrate was immersed therein, upon which there was formed a deposit of 4.1 weight % boron and 95.9 weight % nickel.

10 EXAMPLE II

Another electroless nickel deposition bath was prepared by adding the following to an aqueous bath: 0.3 mol per liter of lactic acid, 0.08 mol per liter of citric acid, 0.04 mol per liter of dimethylamine borane, 0.001 mol per liter of vanadyl sulfate, 0.1 mol per liter of nickel, and a concentration of ammonium hydroxide to raise the bath to a pH of 6.0 at a temperature of 70°C. A deposit composition was formed containing 3.6 weight % boron and 96.4 weight % nickel.

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While in the foregoing specification certain embodiments and examples of this invention have been described in detail, it will be appreciated that modifications and variations therefrom will be apparent to those skilled in this art. Accordingly, this invention is to be limited only by the scope of the appended claims.

CLAIMS:

1. An electroless nickel bath for laying down a nickel-boron deposit, said bath comprising:
  - 5 a bath-soluble source of nickel and
  - a bath-soluble borane reducing agent; andbeing characterized in that it includes zirconyl ions, vanadyl ions, or a combination or mixture thereof.
- 10 2. An electroless bath according to claim 1, wherein the said ions derive from the compound zirconyl chloride, vanadyl sulfate, sodium metavanadate, or a mixture thereof.
3. An electroless bath according to claim 2, wherein  
15 said compound is included within the bath at a concentration of at least about 0.0005 mol per liter, based on the total bath value.
4. An electroless bath according to claim 1, claim 2 or  
20 claim 3, wherein said reducing agent is an amine borane or a cyclic amine borane, present within the bath at a concentration of at least about 0.001 mol per liter, based on the total bath volume.
- 25 5. An electroless bath according to any one of the preceding claims, wherein said bath further includes a complexing agent at a concentration of at least about 0.0005 mol per liter, based on the total bath volume.

6. An electroless bath according to claim 5, wherein said complexing agent is a carboxylic acid or hydroxy substituted carboxylic acid or a bath soluble derivative of either, or an organophosphoric compound.
- 5 7. An electroless bath according to claim 5, wherein said complexing agent is an ester complex of an oxyacid and a polyhydric acid or alcohol.
- 10 8. An electroless bath according to any one of the preceding claims which further includes at least one of a stabilizer, a buffer and a codeposition enhancer.
9. An electroless bath according to any one of the  
15 preceding claims which is at a pH of less than 13.
10. An electroless bath according to claim 9 which is at a pH of between about 4 and about 10.
- 20 11. An electroless bath according to claim 10 which is at a pH of between about 5 and about 7.
12. A method for electrolessly plating with a nickel-boron deposit, comprising immersing a substrate into an electroless  
25 nickel bath and depositing a high-boron-content nickel-boron deposit thereon, said bath being according to any one of the preceding claims.

13. A method according to claim 12, wherein said bath is at a temperature of not greater than 90°C.

14. A method according to claim 12 or claim 13, wherein  
5 said depositing step lays down a deposit including at least about 2 weight % boron, based on the total weight of the deposit.

15. A method according to claim 14, wherein said  
10 percentage of boron is as great as about 5 weight %, based on the total weight of the deposit.

16. An electroless nickel-boron deposit onto a substrate,  
said deposit having been laid down by immersing a substrate  
15 into an electroless bath according to any one of claims 1 to 11.

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## EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 82304210.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	GB - A - 1 360 592 (RCA CORPORATION)  * Claims * --	1,12	C 23 C 3/02
Y	GB - A - 2 066 857 (VMEI "LENIN", QUARTAL DARVENITZA) (15-07-1981)  * Example 2; claims * --	1,4,9-12	
Y	US - A - 4 019 910 (G.O. MALLORY, JR.)  * Column 3, lines 32-53; examples 1,3-5,9,10,13; claims * --	1,4,9-11,12	
Y	US - A - 4 139 660 (W. TUR)  * Column 4, lines 37-44; table I; claims 1-13 * --	1-3,12	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)  C 23 C 3/02
Y	US - A - 4 151 311 (N. FELDSTEIN)  * Column 4, lines 9-51; examples 1,2; claims * --	1-3,6,7,12	
X	US - A - 4 167 416 (B. ZOLLA)  * Totality; especially claims * --	1-3,12	
Y	US - A - 4 259 376 (N. FELDSTEIN) (31-03-1981)  * Column 4, lines 7-48; examples 1,2; claims * --	1-3,12	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-11-1982	Examiner SLAMA
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	DE - B - 1 198 167 (E.I. DU PONT DE NEMOURS AND COMPANY) * Examples; claims * -----	1,4,6, 10-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )